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(19) (CA) **CANADIAN PATENT** (12)

(54) Stabilised Compositions Containing Behaviour
Modifying Compounds

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*pheromone encapsulated in stabilizer
to aid of UV protection - The invention
is the encapsulation of pheromone in a diameter
of 1-100 μ m - pheromone in stabilizer = tertiary
polyamines used here - also using technique of spraying
no teaching of dehydration & rehydration.*

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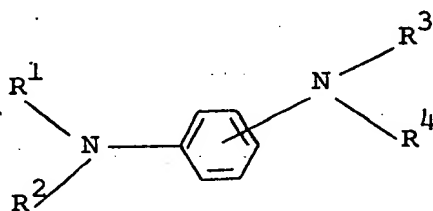
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ABSTRACT

"STABILISED COMPOSITIONS CONTAINING BEHAVIOUR MODIFYING COMPOUNDS"

Compositions containing insect behaviour modifying compounds containing carbon-to-carbon unsaturation, e.g. pheromones, are stabilised by the addition of a tertiary phenylene diamine of formula:



wherein R^1 represents an aromatic residue, R^2 represents H or an alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkaryl, aralkyl, aryl, acyl, acyloxy or nitroso group and R^3 and R^4 , which may be the same or different, each represents an alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkaryl, aralkyl, aryl, acyl, acyloxy or nitroso group.

These compositions are usefully enclosed in microcapsules for spraying in an area of insect infestation in order to disrupt mating patterns, and the invention particularly applies to microencapsulation of the compositions in polyureas, the tertiary phenylene diamines having the advantage that they do not react with the diisocyanate monomer during the microencapsulation process.

DESCRIPTIONTITLESTABILISED COMPOSITIONS CONTAINING
BEHAVIOUR MODIFYING COMPOUNDS

This invention relates to behaviour modifying compounds and is particularly concerned with the stabilisation of photodegradeable compounds of this type.

Some of the most potent behaviour modifying compounds known to man are the so-called pheromones. These may be defined as compounds which are secreted by one member of an animal species which can influence the behaviour or development of another member of the same animal species. Considerable study has been made of pheromones secreted by various insect species, the term "insect" being used here in its broad popular sense. More particularly, the pheromones of various species of moth have been investigated and these have been found to be long chain aliphatic alcohols, esters or aldehydes containing one or more sites of carbon to carbon unsaturation. The compounds are particularly potent in that extremely small quantities of these pheromones are able to bring about the behavioural modification in another member of that species over prolonged distances.

It is frequently found that these pheromones are secreted by members of one sex of the insect species and are able to influence the behaviour of members of the opposite sex of that species and that the pheromones can



consequently be involved in the identification of members of the opposite sex of the species over prolonged distances. Many pheromone studies have been made in relation to insect species where, usually at the larval stage of development, the species acts as a pest on agricultural crops so that, in principle, the pheromone's property can be used as a method of insect control by controlling mating of the species.

Pheromones can therefore be used to bait traps during the mating season of the selected species by utilising an attractant pheromone (or a synthetic analogue thereof which mimics the activity of an attractant pheromone), to lure, usually the male, into the trap during the mating season and so prevent mating. More importantly, mating can be prevented by permeating the atmosphere with the sex pheromone or one of its components or synthetic analogues thereof, thus preventing male and female insects from locating one another. Consequently, subsequent damage to the crop by infestation at the larval stage can be minimised.

The practical implementation of pheromones in the field for insect control has not been entirely straightforward because usually, the naturally occurring pheromones, and synthetic analogues thereof, include one or more sites of carbon to carbon unsaturation which normally means that the compounds are highly susceptible to photodegradation. This means that while the full potency of the pheromone is exhibited initially, the potency is rapidly lost after

exposure to sunlight.

One method which has been successfully used for the stabilisation of photodegradeable compounds, which are to be used agriculturally, is micro-encapsulation.

- 5 Micro-encapsulation techniques are now well developed and enable photodegradeable biologically active compounds, including pheromones, to be contained within the walls of the micro-capsules which are prepared of an appropriate polymeric compound. The micro-capsules are usually
- 10 spherical capsules having a diameter in the range of about 1 to 100 microns and the product frequently takes the form of a suspension of micro-capsules in a continuous aqueous phase so that the suspension can be supplied e.g. by spraying, to the locus to be protected.

- 15 The micro-encapsulation of biologically active compounds, including pheromones, has been recognised to give rise to many advantages, for example the micro-capsule affords a certain measure of physical protection for the biologically active substance and permits a uniform coverage of the locus
- 20 to be protected by, for example, spraying the micro-encapsulated product to give a surface coating on the locus from which there will be a slow release of biologically active compound over a prolonged period of time.

- Various polymeric materials have been proposed for
- 25 the production of the micro-capsules including polyamides, polyesters, polycarbonates, polyureas, polyurethanes and gelatine.

Of these, polyureas have proved to be particularly

suitable as they can be readily generated, for example, by a polycondensation between a polyisocyanate and polyamine. One particular way to micro-encapsulate products of this type which are immiscible with water is

5 to emulsify the biologically active compound in an aqueous medium together with a polyisocyanate such as toluene diisocyanate and then to introduce a polyamine such as ethylene diamine whilst vigorously stirring the mixture so that a polyurea forming reaction occurs forming

10 microcapsules which enclose the biologically active component and any other materials to be formulated with the biologically active component.

Such techniques have previously been used for biologically active compounds but unfortunately, it has

15 been found that where the biologically active compound is photodegradeable, e.g. as is the case with an unsaturated pheromone, the microcapsule is unable to protect fully the biologically active compound against the influence of sunlight and consequently, degradation with consequent loss of

20 biological activity rapidly occurs.

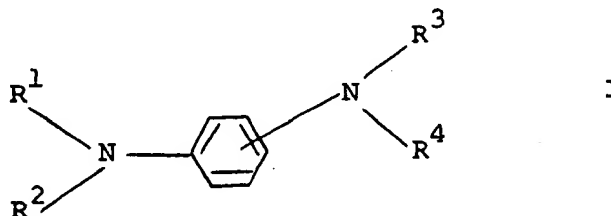
It has been proposed to formulate photodegradeable biologically active compounds with stabilisers, such as polyamines, which are very effective in protecting the biologically active compound against photodegradation

25 but unfortunately, it is not practical to utilise the polyamines hitherto used for stabilisation in cases where

it is desired to present the biologically active material in micro-encapsulated form in a polyurea. This is because the polyamines used hitherto have been primary or secondary polyamines which will react with the diisocyanate during the first stage of the micro-encapsulation process when the stabilised biologically active compound is emulsified with the diisocyanate prior to introduction of the polyamine which will form the polyurea.

We have now discovered that certain tertiary polyamines can be used to stabilise certain behaviour modifying compounds which are susceptible to photodegradation and that such stabilised compositions can be micro-encapsulated in polyurea microcapsules using conventional micro-encapsulation techniques.

According to one aspect of the present invention, there is provided a stabilised composition comprising a carbon-to-carbon unsaturated behaviour modifying compound and, as stabiliser therefor, a tertiary phenylene diamine of formula:



wherein R^1 represents an aromatic residue, R^2 represents H or an alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkaryl, aralkyl, aryl, acyl, acyloxy or nitroso group and R^3 and R^4 , which may be the same or different, each represents

B₁

an alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkaryl, aralkyl, aryl, acyl, acyloxy or nitroso group and in which the behaviour modifying compound is:

- (1) a natural or synthetic insect pheromone
5 containing a mono- or poly- carbon-to-carbon unsaturated hydrocarbon group;
- (2) a said pheromone (1) from a natural source other than a member of an insect species; or
- (3) an analogue and/or isomer of a said
10 pheromone (1) which analogue and/or isomer is prepared synthetically or is from a natural source other than a member of an insect species and itself has insect pheromone activity, the analogue being a) a homologue
15 which is a lower or higher, unbranched or branched alkyl homologue of a said pheromone (1), b) a compound having a greater or lesser number of sites of carbon-to-carbon unsaturation than said pheromone (1) and/or c) a compound in which a $-CH_2CHO$ group in a said pheromone (1) is replaced by $-OCHO$, or in which a $-CHO$ group in a said pheromone (1)
20 is replaced by $-CH_3$ or in which, in a said pheromone (1) which is an alcohol, the alcoholic hydrogen is replaced by a carboxylic acyl group; and the isomer being a) a compound having one or more sites of carbon-to-carbon unsaturation in different position(s) from the position(s)
25 in a said pheromone (1), b) a geometrical isomer of a said pheromone (1) having different configuration(s) at carbon-

to-carbon double bond(s) compared with the said pheromone (1) and/or c) a branched structural isomer of a said pheromone (1).

5 In the compositions of the present invention, it is preferred that the phenylene diamine be a para-phenylene diamine and that R^1 be an aromatic residue of up to 20, e.g. up to 15, carbon atoms, preferably a phenyl group. It is also preferred that at least one of R^2 , R^3 and R^4 be an alkyl group and in the formula I, the alkyl groups, which may be
10 straight or branched chained, preferably contain 1 to 20 carbon atoms. It is also preferred that the alkenyl groups contain 1 to 20 carbon atoms and that the cycloalkyl, cycloalkylalkyl, alkaryl, aralkyl or aryl groups contain up to 20 carbon atoms, particularly up to 15 carbon atoms. A compound of interest
15 is the p-phenylene diamine where R^1 is phenyl, R^2 is H, R^3 is methyl and R^4 is 2-octyl.

When the stabilisers used in the present invention contain alkyl groups, these alkyl groups can be lower alkyl groups such as methyl, ethyl, propyl, isopropyl, or n-, iso-,
20 sec- or tert-butyl or higher alkyl groups such as n- or iso-octyl or n- or branched chain decyl, dodecyl or tetradecyl groups. When the stabilisers used in the present invention contain an acyl or acyloxy group, it is preferred that this will be an alkanoyl or an alkanoyloxy group where the alkanoyl
25 group contains 1 to 20, particularly 1 to 6 carbon atoms, e.g. acetyl or propionyl, or higher groups such as oleoyl or palmitoyl. Although the acyl or acyloxy group will normally

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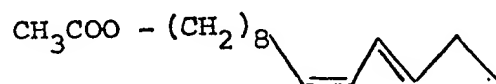
be a carboxylic acyl or acyloxy group of the type mentioned above, it is also possible to use acyl or acyloxy derivatives of sulphonic or phosphoric acids.

One preferred sub-class of stabiliser which can be used in the present invention are the compounds of formula I wherein R^1 represents phenyl, R^2 and R^3 which may be the same or different, each represents a C_1 to C_{20} alkyl, alkenyl or aralkyl group or a C_1 - C_6 acyl or acyloxy group or a nitroso group and R^4 represents a C_7 to C_{20} alkyl group or a phenyl group. It is preferred that these compounds are paraphenylene diamines and typical examples of the C_1 to C_{20} alkyl groups, which are preferably C_1 to C_6 alkyl groups, are the lower and higher alkyl groups mentioned above and typical C_7 to C_{20} alkyl groups are the higher alkyl groups mentioned above. The alkenyl groups preferably contain up to 6 carbon atoms e.g. allyl. A particularly preferred compound of formula I for use in the present invention is the compound where R^1 is phenyl, R^2 and R^3 are each methyl and R^4 is 2-octyl as this compound is liquid at room temperature and consequently can be formulated into these compositions at higher concentrations than can the solid tertiary amines.

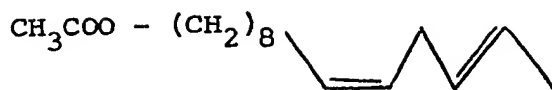
The stabilisers can be prepared by conventional methods, for example, by introducing groups R^2 and R^3 into the corresponding secondary phenylene diamines which are commercially available compounds. For example, when it is desired to introduce alkyl groups R^2 and R^3 into N-2-octyl-N'-phenyl-p-phenylene diamine, the secondary

amine may be alkylated conventionally, e.g. by introducing the desired alkyl halide together with an appropriate base. Similarly, when it is desired to produce compounds including a nitroso or acyloxy group, these can be prepared by nitrosation or by
 5 acylation of the appropriate substituted hydroxy compound.

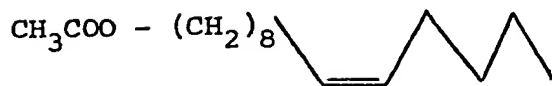
This invention is particularly designed for use with behaviour modifying compounds containing carbon-
 10 to-carbon unsaturation which are to be micro-encapsulated in polyurea micro-capsules. More specifically, the present invention is particularly applicable to formulation of the pheromone components of the Egyptian Cotton Leaf Worm (Spodoptera littoralis). This species is notorious in
 15 that the larvae are responsible for causing considerable damage to cotton crops and consequently, such damage could be reduced by an effective method of controlling this species utilising the pheromone to interfere with normal mating and so reduce larval infestations. It has been
 20 known for several years that three pheromones can be produced by this species, attractant components of formulae III and IIIa and an inhibitory component of formula IV



III



IIIa

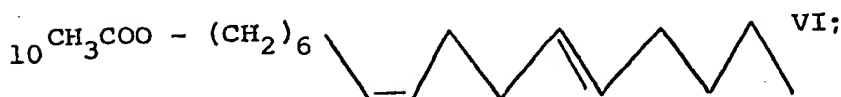


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Other pheromones which can be formulated in accordance with the present invention are the female sex attractant of: the pink boll worm (Pectinophera gossypiella) which has been found to have two attractant components, compounds V and VI,

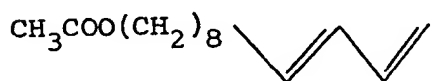


V

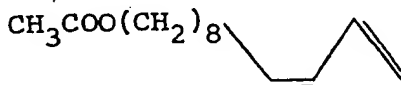


VI;

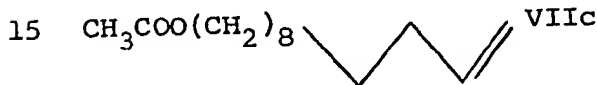
the red boll worm (Diparopsis castanea) which has three attractant components VIIa, VIIb and VIIC and an inhibitory component, VIII,



VIIa



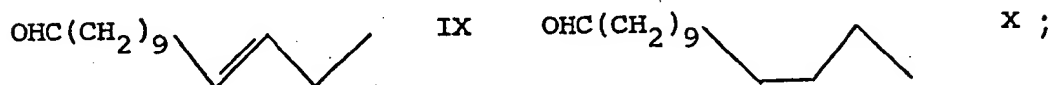
VIIb



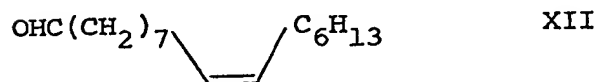
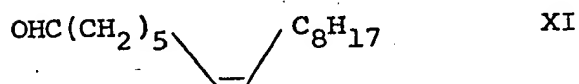
VIIC



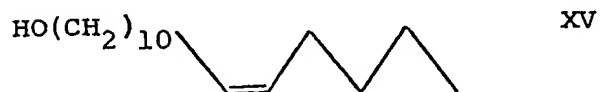
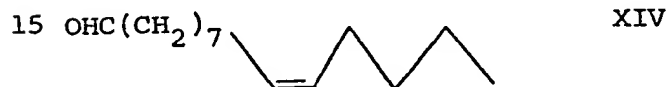
the spruce bud worm (Choristoneura fumiferana) which has two components, IX and X,



5 the corn ear worm (Heliothis zea) which has three unsaturated components XI - XIII,



10 and one saturated component, hexadecanal; and the tobacco bud worm (Heliothis virescens) which has all four components found in Heliothis zea and, in addition, a saturated component tetradecanal and two unsaturated components XIV and XV,



The present invention is applicable not only to the formulation of pheromones but also to the formulation of so-called analogues of said pheromones for example, the compounds of formula XVI and XVII,

5



which exhibit pheromone activity in relation to the rice stem borer (Chilo suppressalis) which itself has natural pheromones of formula XVIII and XIX,

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The present invention may be used in relation not only to naturally produced but also synthetically produced unsaturated behaviour modifying compounds. The above-identified pheromone components may be used singly or as mixtures in the compositions of the invention provided that at least one unsaturated behaviour modifying compound is present. Preferably the mixtures used correspond as closely as possible to the natural blend.

The term "behaviour modifying compound" as used in relation to this invention means:

(i) a compound secreted by a member of an insect species which can influence the behaviour of a member of the same or a different insect species;

(ii) a said compound (i) when prepared synthetically or a said compound (i) from a natural source other than a member of an insect species;

(iii) an analogue and/or isomer of a said compound (i), which analogue and/or isomer is prepared synthetically or is from a natural source other than a member of an insect species and itself can influence the behaviour of a member of an insect species.

In the above definition, "insect" is used in its broad popular sense. It includes within its scope members of the class Insecta, but is not restricted to these.

The term "analogue" in part (iii) of the above definition, means a) homologues i.e. lower and higher unbranched or branched alkyl homologues of said compounds (i), b) compounds having a greater or lesser number of sites of carbon-to-carbon unsaturation than said compounds (i), and/or c) compounds containing a modification of the functional group of a said compound (i), e.g. in which a $-CH_2CHO$ group, in a said compound (i) is replaced by $\overset{*}{O}CHO$, or in which a CHO group in a said compound (i) is replaced by CH_3 , or in which the hydroxyl group in an alcohol compound (i) is replaced by an acyloxy group.

The term "isomer" in part (iii) of the above definition, means preferably compounds having one or more of the sites of carbon-to-carbon unsaturation in different positions from the positions in a said compound (i) and geometrical isomers

i.e. isomers having different configuration at a carbon-to-carbon double bond or bonds compared with a said compound (i). Also preferred are structural isomers involving chain branching.

5 The relative proportions of the stabiliser and of the behaviour modifying compound in the compositions of the present invention are not particular critical and depend upon, inter alia, the extent of photoinstability of the active compound, the effectiveness of the stabilisers and the conditions
10 under which the stabilised composition is to be used in the field. In general, it is found that the amine stabiliser should comprise about 10% to about 1,000% by weight of the behaviour modifying compound and our preliminary experiments have shown that very satisfactory results can be obtained using
15 the two components of the composition in a 2:1 relationship to one another by weight. It is frequently found that the weight of stabiliser in the stabilised composition should be at least as great as that of the behaviour modifying compound in order to achieve optimum stabilisation and reduce, as far as it
20 is possible, the number of occasions on which the stabilised composition needs to be applied to the locus to be protected. On the other hand, the use of excessive proportions of stabiliser is to be avoided as this is both unnecessarily expensive and also increases the volume of stabilised composition which needs to
25 be used. Consequently, it will normally be found that the

stabiliser comprises 50% to 500% by weight of the behaviour modifying compound.

In addition to containing the active compound and a stabiliser, the compositions of the present invention may also include further components which are designed to improve the physical or biological properties of the composition. For example, it has frequently been proposed to incorporate dark-coloured dyestuffs or pigments, the latter in the form of a dispersion, in the formulation of photodegradeable compounds in an attempt to minimise the photodegradation by masking the active photodegradeable compound from sunlight, and the compositions of the present invention may include dark coloured dyestuffs or pigments for this purpose. Typical dyestuffs that may be used include "Waxoline Blue" (colour index - solvent blue 36), "Waxoline Violet" (colour index - solvent violet 13), "Waxoline Black" (carbon black/solvent blue 36/solvent yellow 14/solvent red 24 mixture) or other similar solvent dyestuffs. A suitable pigment is a carbon black pigment dispersed in a hydrocarbon solvent. The composition may also include other stabilisers or surface active compounds in order to modify or improve the subsequent micro-encapsulation process and also other biologically active materials to supplement or potentiate the activity of the behaviour modifying compound. The composition may also include a solvent,

e.g. an alkylbenzene, to solubilise the other ingredients and to improve the efficiency of the emulsification step during subsequent microencapsulation.

According to a further aspect of the present invention, there is provided a micro-encapsulated product comprising a suspension of polymeric microcapsules in an aqueous medium, the microcapsules containing an unsaturated behaviour modifying compound as hereinbefore defined and a tertiary phenylene diamine of formula I as defined above. The active composition contained inside the microcapsules may, for example, contain behaviour modifying compounds and stabilisers of the type specifically exemplified above.

The polymeric microcapsule which contains the active composition of the present invention may be any of the polymeric materials conventionally used for the micro-encapsulation of biologically active material. As mentioned above, the present invention is particularly designed for use in relation to polyurea microcapsules and, in accordance with a still further aspect of the present invention, there is provided a method of preparing a micro-encapsulated product which comprises emulsifying a diisocyanate, an unsaturated behaviour modifying compound and a tertiary phenylene diamine of formula I in an aqueous medium and subsequently introducing into the agitated emulsion a primary or secondary polyamine that will react with the diisocyanate to form a polyurea.

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An alternative method of introducing the polyamine is to add it as a salt e.g. the hydrochloride, and then generate the free amine by adding a base. This may improve the stabilisation of behaviour modifying compounds that are aldehydes.

Although the present invention is particularly designed for use in relation to polyurea microcapsules, the principle of the present invention is applicable to the production of microcapsules from any polymeric material, although major advantages are to be secured when the polymeric material is one derived from a primary or secondary amino component. Other polymeric materials which can be used to formulate microcapsules of the present invention include polyamides, polyesters, polycarbonates and polyurethanes. The techniques generally employed for the production of the microcapsules are conventional interfacial condensation polymerisations, for example, as described in P.W. Morgan "Condensation Polymers by Interfacial and Solution Methods", published 1965 by Interscience. In general, the microcapsules are formed by a polycondensation reaction, e.g. between the diisocyanate and diamine in an aqueous phase under conditions of substantial agitation whereby the polymer is produced in the form of substantially spheroidal particles of diameter 1 to 100 microns and containing the stabilised composition of the invention. The ratio of the weight

- 17 -

of the polymer-forming components (i.e. the monomers) to that of the material to be encapsulated will depend upon the nature of the microcapsule required and, particularly, on the wall thickness required which in turn
5 controls the release rate of the stabilised composition of the invention, but the selection of appropriate wall thicknesses and appropriate microcapsule sizes is well within the competence of the art and reference may be made to any one of the numerous available publications
10 relating to the micro-encapsulation art. However, a ratio of monomers to material to be encapsulated in the range of 0.1:1 to 3:1 has been found to be generally satisfactory.

According to one specific procedure, a solution
15 of the behaviour modifying compound with solvent(s), antioxidant(s), UV absorber(s) etc. as required, together with the oil soluble monomer(s) is emulsified in water with the aid of suitable emulsifiers and high shear mixers. When the desired emulsion droplet size has been obtained,
20 the water soluble monomer(s) are added and mixing continued until the reaction is complete. Any excess monomer or other acid acceptor is neutralised by the addition of acid, and anti-settling agents, wetting agents etc. can be added as desired. The emulsion droplet size
25 largely controls the capsule size which is normally in the range 1-100 micron, preferably 1-5 micron, since the small

microcapsules give better adhesion and retention when sprayed onto foliage. If desired, water soluble by-products can be removed by filtration or centrifugation of the suspension and the micro-capsules can then be
5 redispersed in an aqueous medium.

The rate of release of core material by diffusion through the capsule wall is controlled by the wall thickness i.e. the relative amounts of internal phase and polymer, and by the nature of the polymer i.e. its permeability.

10 Following micro-encapsulation of the stabilised composition of the invention, a sprayable liquid formulation is produced from which the biologically active material may be uniformly applied to the locus where it is desired to bring about behaviour control of the species involved.

15 It is found that the micro-encapsulated product of the present invention exhibits the conventional storage stability properties of micro-encapsulated biologically active materials and can be applied e.g. by spraying, using techniques conventional for the application of micro-encapsulated
20 materials. Consequently, in accordance with a still further feature of the present invention, there is provided a method of influencing the behaviour of a member of an insect species which comprises applying to a selected locus a stabilised composition according to the present invention or
25 a micro-encapsulated stabilised composition according to

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the present invention. As will be readily appreciated,
this aspect of the present invention is particularly
applicable to the spraying of the stabilised composition
or encapsulated stabilised composition on to growing crops
5 so as to interfere with the normal mating of an insect
species which, at at least certain stages of its development,
acts as a pest on agricultural crops.

The following Examples are given to illustrate
the present invention:

EXAMPLE 1N,N'-Dimethyl-N-2-octyl-N'-phenyl-p-phenylene diamine

125 gm (2.5 mole) of 50% sodium hydride dispersion is washed free of mineral oil with petroleum ether and added to
5 a solution of 296 gm (1 mole) of N-2-octyl-N'-phenyl-p-phenylene-diamine (UOP 688) in 1500 ml dry dioxan. The slurry is stirred and heated at reflux for 2 hours and then allowed to cool. 75 ml (1.2 mole) methyl iodide is then added dropwise to the stirred slurry and there is an exothermic reaction. The
10 mixture is then stirred and heated to reflux for 3 hours before cooling and adding a further 75 ml (1.2 mole) methyl iodide.

The cooled reaction mixture is quenched carefully with cold water. When all excess sodium hydride has been
15 destroyed, 5 l of water is added and the phases separated. The lower, aqueous layer is washed twice with 250 ml petroleum ether, and the combined organic extracts are washed twice with 250 ml brine and dried over potassium hydroxide pellets. The solution is filtered through 100 gm neutral
20 alumina and washed through with a further 200 ml petroleum ether. Solvents are removed on a rotary evaporator until the residue reaches constant weight (310 gm).

The product is a pale brown oil that darkens on exposure to light. It shows no reaction with toluene
25 di-isocyanate after 16 hours at room temperature unlike UOP 688 which reacts exothermically with toluene di-isocyanate, and

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there is no N-H absorption in the infra-red spectrum.

The above reactions can be followed by thin layer chromatography on silica gel developed in chloroform containing 1% acetic acid, the spots being visualised with iodine vapour.

5 Rf's: UOP 688 0.5 (purple spot), monomethyl 0.7 (pink), dimethyl 0.6 (blue).

EXAMPLE 2

The effectiveness of a range of stabilisers was tested by mixing 1 mg of tetradecyl acetate and 1 mg of (Z)-9-tetradecenyl acetate with the stabiliser in a glass petri dish (5 cm diameter) so that the mixture formed a thin film over the base. This was then exposed horizontally on a roof for 24-48 hours, after which the residue was analysed by gas chromatography to determine the relative amounts of tetradecyl acetate and (Z)-9-tetradecenyl acetate. These compounds evaporate at similar rates, and so any difference between the amounts left is a measure of the degradation of the unsaturated compound. In the experiments described below, the result is expressed as the ratio of (Z)-9-tetradecenyl acetate:tetradecyl acetate, so that 1.00 indicates no degradation.

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Expt.	Stabiliser				Amount of Stabiliser	Time	Result
	R ¹	R ²	R ³	R ⁴			
A	-				-	24 hrs.	0.05
	BHT				1 mg	24 hrs.	0.13
B	(no stabiliser)				-	10 hrs.	0.47
	2-octyl	H	H	2-octyl	0.2 mg	"	0.62
	phenyl	H	H	2-octyl	0.2 mg	"	0.90
C	(no stabiliser)				-	43 hrs	0.06
	phenyl	H	H	2-octyl	1 mg	"	0.46
	phenyl	H	H	phenyl	1 mg	"	0.58
	CH ₃	CH ₃	CH ₃	CH ₃	1 mg	"	0.09
	phenyl	CH ₃	CH ₃	2-octyl	1 mg	"	0.13
	phenyl	CH ₃	CH ₃	phenyl	1 mg	"	0.26
D	(no stabiliser)				-	27 hrs	0.28
	phenyl	CH ₃	CH ₃	2-octyl	5 mg	"	0.93
	phenyl	H	H	2-octyl	1 mg	"	0.75
	phenyl	H	H	phenyl	1 mg	"	0.72
E	phenyl	CH ₃	CH ₃	2-octyl	5 mg	25 hrs	0.92
	"	"	"	"	"	65 hrs	0.78
	"	"	"	"	"	113 hrs	0.60
	(no stabiliser)				-	25 hrs	0.14

Expt.	Stabiliser				Amount of Stabiliser	Time	Result
	R ¹	R ²	R ³	R ⁴			
F	(no stabiliser)				-	28 hrs	0.38
	phenyl	H	H	2-octyl	1 mg	"	0.80
	Waxoline black				1 mg	"	0.82

BHT = 2,6-di-tert-butyl-4-methylphenol. The relationship of the amine groups in stabilisers for which R¹, R², R³ and R⁴ values are given in this Example is para in each case.

10 N,N'-dimethyl-N-2-octyl-N'-phenyl-p-phenylene diamine (the product of Example 1) is an oil and hence can be formulated in the composition at a higher concentration than certain of the other N,N'-tetrasubstituted compounds.

EXAMPLE 3

15 Similarly to Example 2, the effectiveness of a range of stabilisers was tested by mixing 1 mg of tetradecyl acetate (14:Ac) and 1 mg of (Z)-9-tetradecenyl acetate (Z9-tda) with 1 mg of a stabiliser in a glass petri dish. This was exposed during daylight hours in London for a total of 60 hours, after which the residue was analysed by gas chromatography. The

20 results are the mean of two replicates and comprise % of tetradecyl acetate (14:Ac) remaining (x%) and % of (Z)-9-tetradecenyl acetate (Z9-tda) remaining (y%). (100-x) then represents the percentage of 14:Ac lost by evaporation and (100-y) represents the percentage of Z9-tda lost by evaporation

25 and degradation. % degradation is thus (x-y) and provides a comparative index of the effectiveness of each stabiliser:

	Stabiliser				% remaining		% degradation
	R ¹	R ²	R ³	R ⁴	14:Ac	Z9-tda	
	(no stabiliser)*				80.0	5.6	74.4
	phenyl	H	H	2-octyl	84.2	77.4	6.8
5	"	CH ₃	CH ₃	"	83.1	75.5	7.6
	"	C ₂ H ₅	C ₂ H ₅	"	77.1	68.2	8.9
	"	nC ₁₀ H ₂₁	nC ₁₀ H ₂₁	"	78.1	65.0	13.1
	"	benzyl	benzyl	"	76.3	65.8	10.5
	"	-CH ₂ CH=CH ₂	-CH ₂ CH=CH ₂	"	76.8	68.0	8.8
10	"	-CH(CH ₃) ₂	CH ₃	"	79.7	69.0	10.7
	"	H	COCH ₃	"	75.9	45.6	30.3

* plus 1 mg chlorinated wax "Cerechlor"

EXAMPLE 4

15 A micro-encapsulated product is prepared from the following composition:-

	% w/v	
(<u>Z</u> , <u>E</u>)-9,11-tetradecadienyl (<u>Z</u> 9, <u>E</u> 11-tda)	2.0	} mixed together to form oil phase solution (1)
acetate or (<u>Z</u>)-9-tetradecenyl acetate (Z9-tda)	2.0	
tetradecyl acetate	2.0	
20 Stabiliser A (N,N'-dimethyl-N-2-octyl-N'-phenyl-p-phenylene diamine)	4.0	
'Waxoline Black' (TM)	1.0	
Toluene diisocyanate	5.8	} mixed together to form aqueous phase solution (2)
polyvinyl alcohol e.g. 'Polyviol MO5/140' (TM)	2.0	
water	30.0	

	% w/v	
ethylene diamine	1.0	} mixed together to form solution (3)
diethylene triamine	2.5	
water	5.0	
5 hydrochloric acid	to pH 7.5	
hydroxyethylcellulose e.g. 'Natrosol 250L' (TM)	0.5	
water	to 100%.	

Solution (1) is emulsified into solution (2) using a vortex shear mixer/emulsifier (e.g. a 'Silverson' (TM)) to give an oil/water emulsion of droplet size in the approximate range 1-5 micron. Solution (3) is then added quickly with stirring and a rapid condensation polymerisation reaction occurs at room temperature. Stirring is continued at a reduced rate for an hour and then the acid is added to lower the pH to 7.5, cooling if necessary. Finally the antissettling agent is added and the batch made up to volume with water. The resulting product is a free-flowing aqueous suspension of microcapsules of polyurea containing the acetate ester. The mean particle size of the microcapsules is in the range of 1 to 5 μm . Control products are prepared by a similar procedure but omitting Stabiliser A or by omitting both Stabiliser A and the dye.

A similar micro-encapsulated product was produced by replacing Z9,E11-tdda/Z9-tda with an identical amount of the attractant components of the pheromone of the pink boll worm i.e. (Z,E)-7,11-hexadecadienyl acetate (Z7,E11-hdda) and (Z,Z)-7,11-hexadecadienyl acetate (Z7,Z11-hdda) in a 1:1 ratio. In that case the saturated component (0.2%) was hexadecylacetate.

Example 5

Micro-encapsulated formulations containing equal amounts of (Z)-9-tetradecenyl acetate (Z9-tda) and tetradecyl acetate (tda), with and without

5 stabilisers, prepared as described in Example 4, were sprayed on to filter paper discs which were then exposed on a horizontal surface of a laboratory roof. Filter paper discs were removed at intervals and

10 extracted with chloroform; the extracts were analysed quantitatively for the two acetates by gas chromatography. As the rates of evaporation for the two acetates would be similar, the difference between the amount of tda and Z9-tda remaining represented the amount of degradation of the unsaturated compound.

15 In experiments with formulations containing no tertiary phenylene diamine or dye as stabilisers, the Z9-tda typically disappeared within 6 days. After correcting for loss by evaporation, this indicated a loss of over 60% due to degradation.

20 In an experiment using a formulation containing N,N'-dimethyl-N-2-octyl-N'-phenyl-p-phenylene diamine, (diamine: Z9-tda 5:1 w/w), degradation was 13% after 13 days. With a similar formulation containing additionally the dye Waxoline Black (diamine:Z9-tda:dye, 5:1:0.5),

25 degradation was 9% after 13 days.

In a further experiment using similar microcapsules but with different wall thicknesses containing the same

diamine and dye the following results were obtained:

	Ratio diamine:Z9-tda:dye	Ratio monomers:internal phase (indication of wall thickness)	Ratio tetradecyl acetate: Z9-tda (at half life of tetradecyl acetate)
	5:1:0.5	0.6:1 1:1	1:0.84 1:0.88
5	2:1:0.5	1:1 1.5:1	1:0.76 1:0.71

These results show the better protection of the pheromones at the higher ratio of diamine.

Example 6

10 In the field in Crete, a micro-encapsulated formulation of the type described in Example 4 and containing equal amounts of Z9-tda and tda stabilised by N,N'-dimethyl-N-2-octyl-N'-phenyl-p-phenylene diamine and Waxoline Black (diamine:Z9-tda:dye, 2:1:0.5) was sprayed

15 on to filter papers attached to lucerne. The filter papers were sampled at intervals and analysed for residual Z9-tda and tda. After 14 days exposure the Z9-tda:tda ratio was unchanged, that is, there was no detectable degradation of the unsaturated compound. With

20 unstabilised formulations sprayed under similar conditions there was typically no Z9-tda remaining after 3 to 6 days indicating degradation of 50% or more.

Example 7

To measure the persistence of stabilised pheromones in microcapsules, the following formulations were sprayed onto filter papers which were stapled to the tops of cotton leaves in the field in Egypt.

The formulations were:-

JF 7363 - as Example 4 formulation with pheromone 9,11 tdda (70% ZE)

JF 7348 - as Example 4 formulation with pheromone Z9 tda

JF 6956 - as JF 7348 but with half wall thickness of microcapsules (by halving amount of toluene diisocyanate and adjusting amounts of polyamines incorporated)

Each formulation (10ml) was mixed with 0.5 litre of water before being sprayed. The results were as follows

Day	JF 7363			total 9,11-tdda 14:Ac
	% 14:Ac	% total 9,11-tdda	% ZE 9,11-tdda	
0	100	100	100	0.56
1	95	66	29	0.39
2	78	38	16	0.27
3	68	24	10	0.19
4	72	21	8	0.17
5	58	9.7	3	0.10
6	51			
7	31			

$t_{1/2}$ (days) 5.4 1.6 0.4

5

Day	JF 6956		
	% 14:Ac	% Z9-tda	Z9-tda 14:Ac
0	100	100	0.75
1	87	88	0.77
2	64	65	0.77
3	82	86	0.80
4	77	80	0.78
5	64	62	0.73
6	62	56	0.67
7	51	44	0.65
8	36	30	0.71
10	30	24	0.67
12	18	12	0.57
18	10	6	0.46

10

 $t_{\frac{1}{2}}$ (days) 6.6 5.6

15

Day	JF 7348		
	% 14:Ac	% Z9-tda	Z9-tda 14:Ac
0	100	100	0.92
1	94	102	1.0
2	79	80	0.94
3	89	88	0.90
4	85	77	0.84
5	86	75	0.80
6	72	56	0.72
7	54	43	0.73
8	69	54	0.66
10	53	39	0.69
12	45	31	0.65
18	25	16	0.58

20

25

 $t_{\frac{1}{2}}$ (days) 8.5 6.6

From the above results, it can be seen that the monoene Z9-tda was more persistent than the diene 9,11-tdda, disappearing at a rate similar to that of the saturated compound 14:Ac. This indicates that little of the loss of Z9-tda is due to degradation of the pheromone. Disappearance of both monoene and saturate was marginally faster for the thinner-walled capsules JF 6956 ($t_{1/2}$ = 5.6 and 6.6 days respectively) than the thicker walled capsules JF 7348 ($t_{1/2}$ = 6.6 and 8.5 days respectively). The diene 9,11 tdda had almost disappeared after 6 days exposure and the thermodynamic equilibrium mixture of the geometric isomers was reached in 2 days. No isomerisation of the monoene 9-tda was detected.

As similar experiment was carried out later, also in the field in Egypt, on formulation JF 7518 (as Example 4 formulation but with pheromone 7,11-hdda (1:1 ZE/ZZ) and saturated component (0.2%) hexadecylacetate) with the following results:-

Day	% 16:Ac	% 7,11-hdda	$\frac{7,11-hdda}{16:Ac}$
0	100	100	6.1
2	74	72	5.9
4	57	56	5.9
5	72	48	4.0
7	63	31	3.0
9	37	14	2.5
11		8	1.1
13		4	0.9

10 $t_{\frac{1}{2}}$ (days) 4.2

There was no detectable isomerisation after 13 days

Example 8

Further experiments were carried out in Egypt to measure the persistence of stabilised pheromones in micro-capsules. The formulations studied were:

15 JF 7574 (control) - as Example 4 formulation with pheromone Z9-tda but only 1% w/v of tetradecylacetate (14:Ac), no stabiliser and no dye.

JF 7572 (control) - as JF 7574 but including 1% w/v black dye.

20

JF 7573 - as JF 7572 but including 4% w/v stabiliser A.

JF 7348 (I) } see Example 7, (I) taken to Egypt by land rover,
JF 7348 (II) } (II) taken to Egypt by air

JF 7518 - see Example 7

25 JF 7363 - see Example 7

Each formulation (10 ml) was added to 50 ml water using a Mini-Ulvar sprayer and sprayed uniformly onto filter papers stapled in a regular pattern to square sheets of expanded polystyrene. Each sheet was split diagonally and the two halves fixed horizontally on a roof in Cairo so that the filter papers on one half faced upwards (exposed) and those on the other half faced downwards (shielded) about 1 m from the roof surface. At intervals, for each formulation, two randomly selected discs were removed from the exposed surface and two from the shielded surface and subsequently analysed.

Residual pheromone was extracted with chloroform containing a suitable internal standard for \geq 12 hours at room temperature and analysed quantitatively by gas chromatography.

In respect of both exposed and shielded samples, measurements were taken for JF 7574, JF 7572, JF 7573, and JF7348 (I) and (II) in respect of % 14:Ac and % Z9 tda and for JF 7363 in respect of % 14:Ac, % total 9,11-tda and % ZE 9,11-tda. Measurements for JF 7518 were taken of % 16:Ac and % 7,11-hdda (1:1 ZE/ZZ). From these, half lives for the pheromones in the active formulations were calculated as follows:

HALF LIFE (DAYS)						
Formulation (JF)	Field (see Ex. 7)		Exposed		ROOF	
	sat	phero	sat	phero	sat	phero
6956	6.6	5.6				
7348(I)	8.5	6.6	9.0	7.0	>20	>20
7348(II)			8.0	6.7	>20	>20
5 7363	5.4	0.4*	5.5	<1*	>20	6*
		1.6†		2.1†		19†
7518		4.2	5.8	4.0	>20	>20
7572			4.1	2.5	>20	>20
7573			3.0	2.2	>20	>20
10 7574			4.0	0.6	>20	8.1

sat = saturated component (14:Ac or 16:Ac)

phero = pheromone

* (ZE)-9,11-tdda

† total-9,11-tdda

15 In the roof experiments, disappearance
of the saturated component from exposed JF 7574 (no dye,
no stabiliser) was less rapid ($t_{1/2}=4.0$) than the disappearance
of the pheromone ($t_{1/2}=0.6$) due to light-induced degradation
of the unsaturated component. The fact that the light-stable
20 saturated component disappeared more quickly from exposed
than from shielded samples is attributed to degradation of
the microcapsule walls.

The dye present in JF 7572 reduces degradation of the unsaturated component while the degradation of the saturated component is similar to that in JF 7574 indicating that the dye has little effect on preventing microcapsule wall degradation.

Although the results with JF 7573 are satisfactory and roughly comparable with the JF 7572 results, greater half lives are obtainable when a stabiliser and a dye are present, c.f. JF 7348.

The results for JF 7518 and JF 7363 agree well with those for the same formulation sprayed on filter papers stapled to leaves at the tops of cotton plants in the field (see Example 7). It seems clear that the long-term persistence of the biological effects of each of these (see Examples 9 and 10) may depend to a considerable extent on shielding from sunlight by the plant either by spraying well down in the crop or by new growth effecting shielding.

Tests were also carried out in Brazil on a formulation JF 7546 + JF 7518 (JF 7546 being identical to JF 7518 but with no saturated compound 16:Ac). The $t_{\frac{1}{2}}$ (days) for an unshielded sample was 2 days.

Example 9

Formulations JF 7348 and JF 7363 (see Example 7) were sprayed onto cotton infested with

Spodoptera littoralis in Egypt. These formulations contained, as active component, (Z,E)-9,11-tetradecadienyl acetate (Z9E11-tdda) and (Z)-9-tetradecenyl acetate (Z9-tda), respectively. The effect of the formulations

5 in disrupting communication between male and female S. littoralis was monitored by comparison of catches of the male moth in traps baited with Z9,E11-tdda in areas sprayed with the formulations and in unsprayed control area. The percentage communication disruption on any

10 one night is then the difference between the catch in the treated area and that in the unsprayed control area expressed as a percentage of the latter, complete communication disruption being indicated by 100%. The results were as follows:

Treatment (g acetate ha ⁻¹)	Day	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Z9-tda formulation	\bar{x}	61.7	4.5	10.3	17.3	14.3	3.7	2.7	3.0	0	0	0	0	-	-	-
	%	92.8	75.2	65.5	73.2	91.3	92.9	90.5	100	100	100	100	100	-	-	-
	\bar{x}	26.5	4.0	17.0	21.7	20.0	12.3	4.7	4.3	2.0	3.3	3.3	1.0	-	-	-
Z9Ell-tda formulation	\bar{x}	93.6	59.1	56.8	62.5	71.1	87.6	86.4	90.1	87.3	90.4	95.0	-	-	-	-
	%	57.5	2.0	4.7	6.7	5.7	3.3	4.0	2.7	2.7	1.0	2.0	8.0	-	-	-
	\bar{x}	96.8	88.7	86.7	89.3	92.3	89.5	91.5	86.6	96.2	94.2	59.6	-	-	-	-
Z9Ell-tda formulation	\bar{x}	60.6	0.3	1.0	0.3	0.7	0.7	1.3	0	0	0	0.7	0	0.3	1.0	1.0
	%	99.5	97.6	99.4	98.7	98.4	96.6	100	100	100	100	98.0	100	98.9	97.7	91.9
	\bar{x}	41.7	0.3	2.3	0	0.3	4.0	6.3	6.3	0	2.7	0.7	-	0.3	0	0.7
Controls	\bar{x}	99.5	94.5	100	99.4	90.6	83.4	80.1	100	89.6	98.0	-	-	98.9	100	94.4
	%	43.7	3.7	1.3	21.0	28.0	27.3	10.7	8.3	1.0	7.7	7.7	2.3	6.0	8.7	4.3
	\bar{x}	94.1	96.9	58.2	47.6	35.9	71.8	73.7	95.0	70.4	77.6	88.4	78.9	80.1	65.3	-
Controls	\bar{x}	62.4	62.2	41.6	50.2	53.4	42.6	38.0	31.6	20.2	26.0	34.4	19.8	28.4	43.8	12.4

\bar{x} = mean number of *S. littoralis* male moths caught per trap per day
 % = % disruption in terms of numbers caught relative to controls.
 Plot size for this experiment was 0.01 ha.

In a second experiment the Z9Ell-tda formulation was sprayed at two levels on plots of two different sizes. The results were as follows:-

Rate (g acetate ha ⁻¹)	Plot size ha		Day 0	2	3	5	8	10	12	14	16	18	21
19	0.01	\bar{x} %	2.0	0.3 62.5	0.3 -	0 -	0.4 96.3	2.7 92.8	2.7 94.1	4.8 82.2	9.2 87.7	7.3 76.6	11.8 63.5
38	0.01	\bar{x} %	0.7	0 100	0 100	0 -	2.0 81.5	7.3 80.6	10.8 7.5	11.0 59.1	11.8 84.2	8.0 73.7	7.1 78.0
19	0.1	\bar{x} %	0.3	0 100	0 100	0 -	0.6 94.4	1.5 96.0	2.0 95.6	2.7 90.0	2.7 96.4	2.8 90.8	3.6 88.9
38	0.1	\bar{x} %	0.7	0 100	0 100	0 -	1.0 90.7	1.5 96.0	1.8 96.1	3.0 88.8	3.0 96.0	2.0 93.4	3.9 87.9
Control		\bar{x}	0.3	0.8	0.3	0	10.8	37.7	45.9	26.9	74.5	30.4	32.3

Example 10

5 Formulation JF 7518 (see Example 7) was
sprayed onto cotton infested with Pectinophera
gossypiella in Egypt. This formulation contained,
as active component, 7,11-hexadecadienyl acetate
(7,11-hdda-1:1 ZE/ZZ). The effect was monitored
in the same way as in Example 9, the traps being
baited in this case with the compound sprayed
(7,11-hdda). Results were as follows for 0.01 ha
plots:-

DAY	CONTROL \bar{x}	MICROCAPS					
		2.5g/ha		5g/ha		10g/ha	
		\bar{x}	%	\bar{x}	%	\bar{x}	%
5	0	2.8	4.5	0.2		2.3	
	1	6.4	7.7	3.0		8.3	
	2	3.2	3.7	0.3		5.3	
	3	2.4	6.7	0.3		4.3	
	4	3.0	9.3	3.7		5.0	
10	5	0.7	0	0	100	0	100
	6	0.5	0	0	100	0	100
	7	0.5	1.0	0	100	0	100
	8	10.7	1.3	0	100	0.3	97
	9	4.8	1.7	0	100	0	100
	10	7.0	1.0	2.0	71	0.7	90
	11	5.5	2.0	0.3	95	0.3	95
	12	7.2	2.7	1.0	86	1.0	86
15	13	7.7	0.7	0.7	91	1.3	83
	14	6.2	4.0	1.0	84	3.0	52
	15	15.7	3.3	0	100	1.0	94
	16	8.5	3.3	1.7	80	1.3	85
	17	5.3	9.3	0.7	87	4.3	19
	18	17.0	10.0	1.3	92	3.7	78
	19						
20	20	16.7	5.2	0.7	96	3.8	77
	21	32.1	9.0	3.0	91	4.0	88
	22						
	23	26.8	9.2	3.7	86	2.0	93
	24	18.0	16.7	2.7	85	6.7	63
	25	24.2	17.0	3.0	88	7.7	68
	26	36.5	11.7	11.0	70	19.7	46
30	27	36.7	26.3	7.0	81	12.0	67
	28	32.0	33.0	6.0	81	11.3	69
	29						
	30	28.9	36.0	9.2	68	10.5	64

35 \bar{x} = mean no. of P. gossypiella male moths caught per trap per day

% = % disruption in terms of numbers caught relative to controls

DAY	CONTROL \bar{x}	MICROCAPS 20g/ha		40g/ha	
		\bar{x}	%	\bar{x}	%
5		13.7	1.8	18.7	
		21.7	12.2	32.7	
		10.8	7.5	40.0	
		47.0	11.3	30.7	
	0	24.0	8.3	30.7	
10	1	22.3	0	0	100
	2	17.0	0	0	100
	3	44.0	0	0	100
	4	37.3	0	0	100
	5	34.0	0	0	100
15	6	29.0	0.3	0.3	99
	7	22.0	0	0	100
	8	18.0	0.3	0.3	98
	9	21.0	0	0	100
	10	63.3	0	0.3	99.5
20	11	39.7	0	0	100
	12	29.0	0	0.3	99
	13	66.7	0.3	99.6	0
	14	35.0	0.3	99	0
	15	38.7	0	0.3	99
25	16	97.3	0.7	99	0
	17	66.0	0	0	100
	18	88.0	0	0	100
	19	71.0	0	0	100
	20	45.0	0	0	100
30	21	78.3	0	0	100
	22	118.0	1.0	99.2	0
	23	63.7	0	0	100
	24	65.3	0	1.0	98.5
	25	85.6	0	0.4	99.5
	26	85.6	0	0.4	99.5
	27	177.3	0	0	0
	28	115.0	1.0	99.1	0.3

35 \bar{x} = mean no. of P. gossypiella male moths caught per trap per day

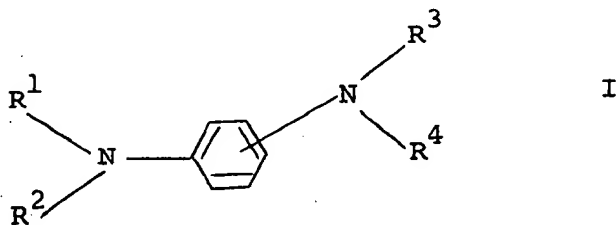
% = % disruption in terms of numbers caught relative to controls.

From these results, it can be seen that the microcapsules at 10g/ha maintained $\geq 90\%$ disruption for 7 days, while at levels of 20g/ha and 40g/ha virtually complete disruption was caused for the 28 days of the experiment - $\geq 98\%$ for the microcapsules at both levels.

Similar tests on the JF 7546 + JF 7518 formulation in Brazil (c.f. Example 8) at 16g/ha showed that this maintained $\geq 90\%$ disruption for 9 days.

The embodiments of the invention, in which an exclusive privilege or property is claimed, are defined as follows:-

1. A stabilised composition comprising a carbon-to-carbon unsaturated behaviour modifying compound and, as stabiliser therefor, a tertiary phenylene diamine of formula:



wherein R^1 represents an aromatic residue, R^2 represents H or an alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkaryl, aralkyl, aryl, acyl, acyloxy or nitroso group and R^3 and R^4 , which may be the same or different, each represents an alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkaryl, aralkyl, aryl, acyl, acyloxy or nitroso group and in which the behaviour modifying compound is:

(1) a natural or synthetic insect pheromone containing a mono- or poly- carbon-to-carbon unsaturated hydrocarbon group;

(2) a said pheromone (1) from a natural source other than a member of an insect species; or

(3) an analogue and/or isomer of a said pheromone (1) which analogue and/or isomer is prepared synthetically or is from a natural source other than a member of an insect species and itself has insect pheromone activity, the analogue being a) a homologue

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which is a lower or higher, unbranched or branched alkyl homologue of a said pheromone (1), b) a compound having a greater or lesser number of sites of carbon-to-carbon unsaturation than said pheromone (1) and/or c) a compound in which a $-CH_2CHO$ group in a said pheromone (1) is replaced by $-OCHO$, or in which a $-CHO$ group in a said pheromone (1) is replaced by $-CH_3$ or in which, in a said pheromone (1) which is an alcohol, the alcoholic hydrogen is replaced by a carboxylic acyl group; and the isomer being a) a compound having one or more sites of carbon-to-carbon unsaturation in different position(s) from the position(s) in a said pheromone (1), b) a geometrical isomer of a said pheromone (1) having different configuration(s) at carbon-to-carbon double bond(s) compared with the said pheromone (1) and/or c) a branched structural isomer of a said pheromone (1).

2. A composition according to claim 1 wherein, in the stabiliser of formula I, R^1 represents phenyl, R^2 and R^3 which may be the same or different, each represents a C_1 to C_{20} alkyl, alkenyl or aralkyl group or a C_1 to C_6 acyl or acyloxy group or a nitroso group and R^4 represents a C_7 to C_{20} alkyl group or a phenyl group.

3. A composition according to claim 1 wherein the stabiliser is an N,N'-dialkyl-N-2-octyl-N'-phenyl-p-phenylene diamine, an N-alkyl-N-2-octyl-N'-phenyl-p-phenylene diamine, an N,N'-dialkenyl-N-2-octyl-N'-phenyl-p-phenylene diamine or an N,N'-diaralkyl-N-2-octyl-N'-phenyl-p-phenylene diamine.

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4. A composition according to claim 3 wherein the stabiliser is N,N'-dimethyl-N-2-octyl-N'-phenyl-p-phenylene diamine.

5. A composition according to claim 1 wherein the stabiliser comprises 50 to 500% by weight of the behaviour modifying compound.

6. A composition according to claim 1 wherein the behaviour modifying compound is: (Z,E)-9,11-tetradecadienyl acetate, (Z,E)-9,12-tetradecadienyl acetate, (Z)-9-tetradecenyl acetate, (Z,E)- or (Z,Z)-7,11-hexadecadienyl acetate, (E)- or (Z)-9,11-dodecadienyl acetate, 11-dodecenyl acetate, (E)-9-dodecenyl acetate, (E)- or (Z)-11-tetradecenal, (Z)-7-hexadecenal, (Z)-9-hexadecenal, (Z)-11-hexadecenal, (Z)-9-tetradecenal, (Z)-9-tetradecenyl formate or (Z)-11-hexadecenyl formate or a mixture of any of these.

7. A composition according to claim 1 which also contains a dark-coloured dyestuff or pigment.

8. A micro-encapsulated product comprising a suspension of microcapsules in an aqueous medium, the microcapsules being of a polymeric material which encapsulates a composition comprising a carbon-to-carbon unsaturated behaviour modifying compound as defined in claim 1, and as stabiliser therefor, a tertiary phenylene diamine of formula I as defined in claim 1.

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9. A micro-encapsulated product according to claim 8 wherein the stabiliser is an N,N'-dialkyl-N-2-octyl-N'-phenyl-p-phenylene diamine, an N-alkyl-N-2-octyl-N'-phenyl-p-phenylene diamine, an N,N'-dialkenyl-N-2-octyl-N'-phenyl-p-phenylene diamine or an N,N'-diaralkyl-N-2-octyl-N'-phenyl-p-phenylene diamine.

10. A micro-encapsulated product according to claim 8 wherein the behaviour modifying compound is (Z,E)-9,11-tetradecadienyl acetate, (Z,E)-9,12-tetradecadienyl acetate, (Z)-9-tetradecenyl acetate, (Z,E)- or (Z,Z)-7,11-hexadecadienyl acetate, (E)- or (Z)-9,11-dodecadienyl acetate, 11-dodecenyl acetate, (E)-9-dodecenyl acetate, (E)- or (Z)-11-tetradecenal, (Z)-7-hexadecenal, (Z)-9-hexadecenal, (Z)-11-hexadecenal, (Z)-9-tetradecenal, (Z)-9-tetradecenyl formate or (Z)-11-hexadecenyl formate or a mixture of any of these.

11. A micro-encapsulated product according to claim 8 wherein the polymeric material of the microcapsule is a polyurea.

12. A process of preparing a micro-encapsulated product as claimed in claim 8, which process comprises emulsifying, in an aqueous medium, a carbon-to-carbon unsaturated behaviour modifying compound as defined in claim 8, a tertiary phenylene diamine of formula I as defined in claim 8 as stabiliser therefor and one or more oil-soluble monomers, agitating the emulsion and adding

thereto one or more water-soluble monomers to effect an interfacial condensation polymerisation forming a polymer which encapsulates the behaviour modifying compound and stabiliser.

13. A process according to claim 12 wherein the oil-soluble monomer is a diisocyanate which is polymerised with a primary or secondary polyamine as water-soluble monomer to form a polyurea.

14. A process according to claim 13 wherein the primary or secondary polyamine is introduced to the reaction in the form of a salt and is generated in the form of its free amine by addition of a base.

15. A method of influencing the behaviour of a member of an insect species characterised by applying to a selected locus a stabilised composition as claimed in claim 1, 3 or 6.

16. A method of influencing the behaviour of a member of an insect species characterised by applying to a selected locus a micro-encapsulated product as claimed in claim 8, 9 or 10.

